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COMPLETE SPECIFICATION

Electroplating on Aluminium and its Alloys

We, W. CANNING AND COMPANY LIMITED, of 133, Great Hampton Street, Birmingham 18, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

THIS INVENTION relates to the electroplating on aluminium and aluminium base alloys.

The immersion of aluminium or its alloys in aqueous alkaline solutions of sodium hydroxide containing sodium zincate as a prior process to subsequent electroplating has been known previously and is termed a "zincate" dip. However, it has previously been found necessary in industrial practice to deposit copper or brass from an alkaline solution, or dull nickel from special types of solution having weak acidity and containing large quantities of alkali metal sulphates, on to the immersion deposit of zinc formed from the "zincate" dip, before attempting to apply a nickel deposit from the standard acidic solutions normally employed for commercial bright nickel plating of steel, brass or copper articles. Otherwise only a poorly adherent nickel coat was obtained from these standard acidic solutions. The use of this additional copper, or brass, or dull nickel, plating operation renders the process for nickel plating, using the standard acidic nickel plating solutions, on to aluminium more complicated and costly than it otherwise would be.

The object of this invention is to eliminate the necessity of these copper or brass or dull nickel plating operations and to provide an alkaline solution containing an alkali metal,

e.g. sodium, zincate, which solution gives an immersion deposit of zinc, on aluminium and its alloys, of a type which allows nickel to be plated directly on to the immersion deposit of zinc on the aluminium or its alloys from acidic nickel plating solutions as normally used commercially, while still giving nickel coatings which have excellent adherence.

The invention consists in an aqueous alkaline solution of an alkali metal zincate, containing a dissolved nickel complex.

The complex will not dissociate in the solution, so that therefore nickel-containing precipitates are not formed; however, it is instrumental in forming a coating, believed to be predominantly zinc, on suitably prepared aluminium, or aluminium alloy, surfaces when these are immersed in the solution according to the invention, and this coating, when e.g. nickel-plated in commercial nickel plating solutions of either the dull or so-called semi-bright or bright types, provides a surface which allows a nickel coat to be deposited which has excellent adhesion to the metal underneath. No intermediate copper or brass plating is needed after this immersion treatment and before nickel plating from standard nickel plating solutions, but only thorough rinsing, e.g. in water or a dip of very dilute sulphuric acid.

The nickel complex can either be formed *in situ* or prepared separately (by the interaction of a soluble nickel salt, e.g. nickel sulphate, nickel chloride or nickel nitrate and a complexing agent, e.g. potassium cyanide and/or (sodium potassium tartrate) before addition to the alkaline solution of the alkali zincate.

In one embodiment the invention consists in an aqueous solution containing:—

nickel sulphate hexahydrate	8 to 45 g/l.
zinc sulphate heptahydrate	20 to 70 g/l.
potassium cyanide	5 to 30 g/l.
sodium hydroxide	80 to 180 g/l.

In a preferred embodiment the solution contains:

nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	20 to 40 g/l.
zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)	30 to 60 g/l.
potassium cyanide	7 to 13 g/l.
Sodium hydroxide	80 to 140 g/l.

5 Up to 45 g/l. of tartaric acid may be added to the above solution.

Alternatively, an amount of an alkali metal salt of tartaric acid (e.g. potassium hydrogen tartrate, sodium potassium tartrate (Rochelle salt) or disodium tartrate) supplying the same amount of tartrate ion as the above may be added.

10 When tartaric acid, or an acid tartrate, is added enough sodium hydroxide or other alkali hydroxide must be added to neutralise it. Other alkali metal cyanides than potassium cyanide may be used providing the requisite quantity of cyanide ions are available for complex formation. Other alkali hydroxides can be used instead of sodium hydroxide in quantities to give the same resultant alkalinity.

15 Zinc oxide, zinc chloride and/or zinc nitrate can be used in place of zinc sulphate if the amount used is sufficient to supply the same quantity of zinc ions in soluble form expressed as metallic zinc.

Other chemicals which may be optionally added to the solution given above are water soluble cupric salts such as copper sulphate or nitrate, soluble ferric salts such as ferric nitrate or chloride and alkali metal nitrates.

20 These chemicals may be added individually or two or more used together provided the conditions given below are fulfilled. Cupric salts to provide up to 2 g/l. of cupric ions or an equivalent amount of the copper-containing complex ions, in the solution may be added. They can be added either as a cupric salt solution in a small volume of water or, preferably, complexed by reaction with an alkali cyanide and/or tartaric acid or an alkali tartrate before addition to the zincate solution. The ferric salts are used in proportions to give up to 1 g/l. of ferric ion, or an equivalent amount of iron-containing complex ions, in the zincate solution. Again

the ferric salts may be added as a concentrated solution in water or else preferably complexed by reaction with tartaric acid or an alkali tartrate before addition to the zincate solution.

The alkali metal nitrates are added to give a concentration of nitrate ion of up to 2 g/l. per litre.

25 The invention further consists in a process for treating a surface of aluminium or aluminium base alloys prior to electrolytically depositing a metal thereon, comprising the steps of: alkaline cleaning of the said surface; acid etching of the said surface; immersion of the surface in the solution as described above in accordance with the invention; and rinsing of the surface with, e.g. water or dilute sulphuric acid.

It is greatly to be preferred and for most practical purposes essential to rinse the surface between the cleaning and etching and between the etching and immersion to prevent carrying over one solution to the next.

30 Preferably, the alkaline cleaning is effected by making the aluminium or its alloy cathodic in an aqueous solution containing trisodium phosphate and sodium hydroxide, e.g. a solution containing 18 oz./gal. of sodium hydroxide and 4 oz./gal. of trisodium phosphate.

35 Preferably again, the acid etching is carried out in an aqueous solution of nitric acid, e.g. containing 50% (v/v).

40 In a modification of the process, the surface is re-etched with acid after immersion in the solution according to the invention, and then re-immersed in the solution, being finally rinsed. Moreover, it may be of advantage to precede the process with a degreasing stage carried out in boiling trichlorethylene liquid and/or vapour.

45 Although this process is especially convenient for nickel plating, it may be used also when electro-plating with other metals, e.g.

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copper, zinc, brass, cadmium, silver, chromium, gold and tin.

The invention still further consists in aluminium and aluminium alloys which have been dipped in the solution according to the invention so that a deposit is formed on the surface, and in articles made from aluminium or its alloys when electroplated after immersion in the solution according to the invention.

The invention will be further described with reference to the following Examples, which are not to be construed as limiting the scope of the claims in any way, with the exception of claims 17, 29 or 30.

EXAMPLE 1:

An aqueous solution containing:—

nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	30 g/l.
zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)	40 g/l.
potassium cyanide	10 g/l.
sodium hydroxide	115 g/l.
potassium hydrogen tartrate	40 g/l.

was contacted with an aluminium surface which had been cleaned by making it cathodic in a solution containing 18 oz./gal. sodium hydroxide and 4 oz./gal. trisodium phosphate, followed by an acid etching in a 50% (v/v) nitric acid solution.

A deposit formed on the surface of the aluminium which when plated in a con-

ventional nickel-plating bath gave a good nickel coat with excellent adhesion to the underlying aluminium.

EXAMPLE 2:

The following aqueous solutions A-F could be used in the method of Example 1:—

Chemical	Solution					
	(in g/l.)					
	A	B	C	D	E	F
Nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	25	30	30	30	30	30
Zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)	40	40	40	48	48	40
Sodium hydroxide	103	115	106	110	110	106
Potassium cyanide	30	10	11	11	11	11
Potassium hydrogen tartrate ($\text{KHC}_4\text{H}_4\text{O}_6$)	—	40	—	—	—	—
Sodium potassium tartrate ($\text{KNaC}_4\text{H}_4\text{O}_6$)	—	—	45	40	40	40
Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	—	—	5	—	—	5
Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)	—	—	—	—	2	2
Sodium nitrate	—	—	—	1	—	1

EXAMPLE 3:

Examples of Process Sequences Found Satisfactory for Aluminium and Various Aluminium Base Alloys.

N.B. If the work is heavily soiled with grease and/or polishing composition, immersion of the aluminium or aluminium base alloy in boiling trichlorethylene liquid and/or the vapour evolved from that liquid may be

necessary to remove this gross contamination, prior to carrying out the sequences shown in the following Table.

The Roman numbers given are the order in which the operations were performed in the process sequence used, with the time for each operation in brackets. Intermediate rinsing of the aluminium or aluminium base alloy in cold running water is necessary

between each of the operations listed in the above process sequences. Thorough rinsing, e.g. in water or dilute sulphuric acid is also essential after the last operation noted above

before immersion of the aluminium or aluminium base article having on its surface zincate film into the nickel electroplating solution. 5

Process Used	Aluminium Alloy							
	Aluminium (99.99%)	B.S.1470 S.1B	B.S.1470 S.1B	B.S.1476 H.E.9.	B.S.1490 L.M.2.	B.S.1490 L.M.6.	B.S.1490 L.M.5.	
Type of Zincate Solution used.	A	B	C	D	E	F	F	F
Immersion in 4 ozs./gall. sodium hydroxide at 160°F.	—	—	—	—	I (30 sec)	—	—	—
Alkali cleaning	I (2 min)	I (1 min)	I (3 min)	I (1 min.)	—	—	—	—
Cathodic treatment in solution containing 18 ozs./gall. sodium hydroxide and 4 ozs./gall. tri- sodium orthophosphate at ambient temperature.	—	—	—	—	II (2 min)	I (2 min)	I (2 min)	I (2 min)
Cathodic treatment in solution containing 3 ozs./gall. sodium hydroxide and 1 oz./gall. tri- sodium orthophosphate at ambient temperature.	—	—	—	—	—	—	—	—
acid etch	II (1 min)	II (30 sec)	II (1½ min)	II (1 min)	III (2 min) V (10 sec)	II (2 min) IV (30 sec)	—	—
Immersion in 15% by volume solution of concentrated sulphuric acid at 150°F.	—	—	—	—	—	—	II (1 min)	—
Zincate Dip	III (1½ min)	III (1 min)	III (2 min)	III (1 min)	IV (30 sec) VI (10 sec)	III (30 sec) V (15 sec)	III (1 min)	—
rinse	—	—	—	—	—	VI (5 sec)	—	—
Immersion in 0.5% by volume solution of concentrated sulphuric acid at ambient temperature.	—	—	—	—	—	—	—	—

Thus, although cyanide and/or tartrate are herein specified as complexing agents, it is not intended to limit the invention to these in any way; any nickel complex which is soluble in the alkaline zincate solution but which is instrumental in forming such an adherent deposit capable of being plated on aluminium or aluminium alloy surface may be used.

10 WHAT WE CLAIM IS:—

1. An aqueous alkaline solution of an

nickel sulphate hexahydrate	8 to 45 g/l.
zinc sulphate heptahydrate	20 to 70 g/l.
potassium cyanide	5 to 30 g/l.
sodium hydroxide	80 to 180 g/l.

5. An aqueous alkaline solution containing:—

nickel sulphate hexahydrate	20 to 40 g/l.
zinc sulphate heptahydrate	30 to 60 g/l.
potassium cyanide	7 to 13 g/l.
sodium hydroxide	80 to 140 g/l.

25 6. An aqueous alkaline solution as claimed in any one preceding claim which also contains up to 45 g/l. of tartaric acid or an alkali metal salt of tartaric acid supplying the same amount of tartrate ion, enough sodium hydroxide being present to neutralise the acid or any acid salt.

30 7. An aqueous alkaline solution as claimed in claim 6 in which the alkali metal tartrate is potassium hydrogen tartrate, sodium potassium tartrate (Rochelle salt) or disodium tartrate.

35 8. An aqueous alkali solution as claimed in claim 4, 5, 6 or 7 modified in that an alkali metal cyanide other than potassium cyanide, and making the same concentration of cyanide ion available for complex formation is present.

40 9. An aqueous alkaline solution as claimed in any one of claims 4 to 8 in which zinc oxide, zinc chloride or zinc nitrate is used instead of zinc sulphate in an amount sufficient to supply the same quantity of zinc ions in soluble form expressed as metallic zinc.

45 10. An aqueous alkaline solution as claimed in any one of claims 2 to 9 modified in that alkaline hydroxides other than sodium hydroxide are used in amounts sufficient to give the same alkalinity.

50 11. An aqueous alkaline solution as claimed in any one preceding claim containing water-soluble cupric salts, water-soluble ferric salts

alkali metal zincate, containing a dissolved nickel complex.

2. An aqueous alkaline solution as claimed in claim 1 comprising sodium zincate, sodium hydroxide and a water-soluble nickel complex. 15

3. An aqueous alkaline solution as claimed in claim 1 or 2 in which the nickel complex is a complex between nickel and cyanide ions. 20

4. An aqueous alkaline solution containing:—

complexes formed with these salts, or alkali metal nitrates.

12. An aqueous alkaline solution as claimed in claim 11 to which has been added copper sulphate or copper nitrate. 60

13. An aqueous alkaline solution as claimed in claim 11 or 12 in which up to 2 g/l. of cupric ions or an equivalent amount of copper-containing complex ions are present.

14. An aqueous alkaline solution as claimed in claim 11, 12 or 13 to which has been added ferric nitrate or ferric chloride. 65

15. An aqueous alkaline solution as claimed in any one of claims 11 to 14 which contains up to 1 g/l. of ferric ions or an equivalent amount of iron-containing complex ions. 70

16. An aqueous alkaline solution as claimed in any one of claims 11 to 15 where alkali nitrates are present, in which up to 2 g/l. of nitrate ion are present. 75

17. An aqueous alkaline solution of an alkali metal zincate containing a dissolved nickel complex substantially as hereinbefore described with reference to any one of the Examples given. 80

18. A process for treating a surface of aluminium or aluminium base alloys prior to electrolytically depositing a metal thereon, comprising the steps of; alkaline cleaning of the said surface; acid etching of the surface; immersion of the surface in the solution as claimed in any one preceding 85

claim; and rinsing the surface free from alkaline solution.

19. A process as claimed in claim 18, modified in that after immersion in the solution as claimed in any of claims 1 to 17, the surface is again etched with acid and re-immersed in the said solution before rinsing.

20. A process as claimed in claim 18 or claim 19 in which the surface is rinsed between the alkaline cleaning and acid etching, and between acid etching and immersion in the said solution.

21. A process as claimed in any one of claims 18 to 20 in which the alkaline cleaning is effected by making the aluminium or its alloy cathodic in a sodium hydroxide/trisodium phosphate solution.

22. A process as claimed in any one of claims 18 to 20 in which the acid etching is carried out in an aqueous solution of nitric acid.

23. A process as claimed in any one of claims 18 to 22 when preceded by a degreasing stage.

24. A process as claimed in any one of the preceding claims 18 to 23 which includes the step of preparing the nickel complex separately and adding it to the alkali metal zincate solution.

25. A process as claimed in any one of the preceding claims 18 to 23 which includes

the step of forming the nickel complex *in situ* in the alkali metal zincate solution.

26. A process as claimed in any of the preceding claims 18 to 25 wherein the aqueous alkaline solution used is as claimed in any of claims 11 to 17 and in which the cupric or ferric salts are added to the zincate solution containing a dissolved metal complex in the form of a small amount of concentrated aqueous solution.

27. A process as claimed in any one of claims 18 to 25 wherein the aqueous alkaline solution used is as claimed in any of claims 11 to 17 and in which the cupric or ferric salts are added as complexes with an alkali metal cyanide, and/or tartaric acid or an alkali metal tartrate.

28. A process as claimed in any one of claims 18 to 27 when followed by the electrolytic deposition of nickel upon the surface.

29. A process for treating a surface of aluminium or aluminium alloys substantially as hereinbefore described with reference to the Examples given.

30. Articles with a surface treated by the process as claimed in any one of claims 18 to 29.

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